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THE NUCLEAR INDUSTRY: ION EXCHANGE

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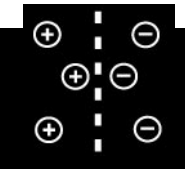

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Introduction

Ion exchange is used in nearly all phases of the nuclear fuel cycle beginning in the early stages of uranium ore treatment where ion exchange is one of the major processes used: uranium is removed from ore leach liquors using anion exchange resins.

At nuclear power plants, ordinary organic ion exchange resins are mainly used for the removal of ionic and particulate contaminants from the primary circuit, condensate and fuel storage pond waters. Ion exchange resins are also used for the solidification of low- and medium-activity nuclear waste solutions. The number of applications of selective inorganic ion exchangers in the separation of radionuclides from nuclear waste solutions has been increasing since the mid-1980s.

In nuclear fuel reprocessing plants, the main separation method is solvent extraction. Ion exchange is, however, used for the solidification of low- and medium-activity waste solutions, as well as for the partitioning of radioactive elements for further use.

This article reviews all the most important areas of the utilization of ion exchangers in the nuclear power industry. Special attention is paid to ion exchange processes, which involve radionuclide removal functions, and to new developments in selective ion exchange materials.

Ion Exchange Materials Used in the Nuclear Industry

Nuclear Grade Ion Exchange Resins

Organic ion exchangers used at nuclear power plants are based on conventional poly(styrene–divinylbenzene) resins with sulfonic acid ($-SO_3^-$) and quaternary ammonium ($-N(CH_3)_3^+$) functional groups for cations and anions, respectively. Nuclear grade resins,

however, have to meet higher quality requirements than those used in most other industries.

First of all, the purity levels of nuclear grade resins have to be very high and, in particular, leachable corrosive impurities such as chloride and sulfate in anion exchange resins should be avoided. Second, nuclear grade resins should have high levels of the desired ionic form. For example, cation exchange resins in the hydrogen form, used in mixed beds for demineralization, should not contain a high proportion of sodium ions because they become activated in the neutron flux of the primary circuit and increase the radiation field. The content of heavy metals should also be very low. Thus, nuclear grade cation exchange resins are usually a minimum of 99% purity in the hydrogen form and typically the sodium and iron contents are below 0.01% and the contents of other metals even lower. ^{7}Li-form resins, used in some pressurized water reactors, have a 99% minimum purity in the lithium form. Nuclear grade anion exchange resins have a 95% minimum in the OH^- form, the rest being mainly in the CO_3^{2-} form. The contents of chloride and sulphate in anion exchange resins are typically very low, less than 0.1% and 0.3%, respectively. In addition to a high purity and a high level of desired ionic form, nuclear grade resins are more uniform in particle size compared with conventional resins and the amount of fines is very low.

Organic ion exchange resins are used in nuclear plants in two ways (**Figure 1**). First, as deep beds, i.e. columns packed with bead form resins. The volume of a bed is typically 1–2 m^3 and the bead size 20–50 mesh. Their second use is as pre-coat filters, i.e. inert filters coated with a layer of crushed anion–cation resin mixture; the layer thickness is typically 5 mm and the particle size 200–400 mesh. Pre-coat filter systems are mainly used in the purification of solutions that contain high proportions of solid matter.

Inorganic Ion Exchangers

Use of inorganic ion exchangers at nuclear plants has been increasing since the mid-1980s. Utilization has been limited in nuclear waste management processes where the main advantage of inorganic ion exchangers over organic exchangers has been their superior selectivities to certain radionuclides. Other advantages are their resistance to radiation and high temperatures. The main problems which have hindered installation of inorganic ion exchange materials have been that they have not been available in stable grains or granules suitable for use in packed bed columns and that many of them are not chemically stable in high or even moderate acidities and alkalinities. As will be seen below, some of these problems have been overcome in the last 10 years.

Ion Exchange in the Processing of Uranium Ores

Uranium ores are first ground into submillimetre particles and uranium is leached out with sulfuric acid. If the ore contains a large quantity of acid-consuming $CaCO_3$, leaching is carried out with sodium or ammonium carbonate solution. In sulfuric acid and carbonate solutions, uranium forms soluble sulfate and carbonate complexes, predominantly $UO_2(SO_4)_3^{4-}$ and $UO_2(CO_3)_3^{4-}$. These anionic complexes are removed from leach liquor with strongly basic anion exchange resins. For further processing, uranium sulfate is eluted from resin with dilute (0.1–1.0 mol L^{-1}) acid solutions. In the case of carbonate leaching, elution from the resin is carried out with dilute sodium chloride or ammonium nitrate solutions instead of acid to prevent formation of carbon dioxide in the column.

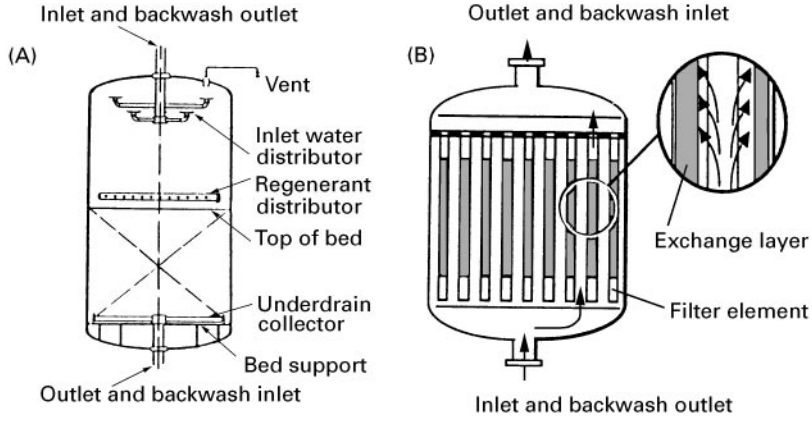

Figure 1 Typical deep bed (A) and pre-coat filter (B) units used at nuclear power plants.

Ion Exchange Processes at Nuclear Power Plants

Ion exchangers are utilized for many purposes at nuclear power plants (NPP):

- Purification of primary coolant water
- Control of primary coolant water chemistry
- Polishing of steam condensate
- Production of make-up water
- Purification of spent fuel storage pond water
- Treatment of waste solutions.

Most of these processes are used in all types of nuclear power plants. Purification of the primary coolant by ion exchange is, of course, not necessary in gas cooled reactors. Control of primary coolant chemistry applies only to some pressurized water reactors (PWR), using both light and heavy water as a moderator/coolant. Polishing of steam condensates is important in all reactor types but only in boiling water reactors (BWR) does it play an important role in removing radioactive contaminants. The two Finnish nuclear power plants, Olkiluoto NPP and Loviisa NPP, are given below as examples of installations using typical ion exchange systems for boiling water and pressurized water reactors. Loviisa NPP uses some 15 tonnes of ion exchange resins per annum and Olkiluoto NPP 22 tonnes.

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Purification of Primary Coolant Water

In nuclear power reactors the primary coolant water is circulated from the reactor vessel to the steam generator (PWR)/turbine (BWR) and back. In BWRs the primary coolant is pure water but in PWRs it also contains boric acid, which is used as a moderator to slow down the neutrons and LiOH or KOH to adjust the pH. Primary coolant water contains radioactive components in ionic and particulate form and these have to be removed to prevent the build-up of excessive radiation fields. There are two types of radioactive contaminants in the primary circuit: fission products originating from leakages from the fuel elements, the most important of these nuclides being ^{137}Cs, and activated corrosion products from reactor materials, of which ^{60}Co and ^{63}Ni are usually the most important (^{51}Cr, ^{54}Mn, ^{58}Co and ^{65}Zn can be found as well). Caesium exists in solution in ionic form and the corrosion products are mainly in the form of particles. In the removal of these radioactive contaminants, ion exchange resins work both as ion exchangers and as mechanical filters.

The exhaustion of the ion exchangers in all the processes at nuclear power plants is determined by one of the following parameters:

- Increased conductivity in the effluent
- Increased radioactivity in the effluent
- Increased pressure drop.

Especially in the processes where large amounts of solid fines are to be removed, increased pressure drop is the dominant parameter.

At the Olkiluoto NPP, which has two 710 megawatt (MW) BWRs, primary circuits are purified with two parallel deep bed units each of 1.5 m^3 volume. The beds consist of equal quantities of cation and anion exchange resins. The function of the ion exchange purification system is to remove all ionic contaminants. The resins are initially in the H^+ and OH^- forms and they demineralize water as shown in eqn [1].

$$RH + ROH + Na^+ + Cl^- \rightleftharpoons RNa + RCl + H_2O \quad [1]$$

where R is the resin matrix. The temperature of the water (270°C) has to be lowered to 60°C before conveying it into the ion exchanger bypass. The flow through each unit is about 2% of the total flow. Resins are replaced twice a year and solidified, without regeneration, with bitumen in the ratio of about 1 : 1 for final disposal.

At the Loviisa NPP, which has two 440 MW PWRs, the primary circuits are purified by two independent ion exchange systems. The first one is a deep bed having 1 m^3 of equal amounts of cation and anion resins. The second system consists of two beds, of 1 m^3 each, one being a cation exchanger and the other an anion exchanger. In both systems the exchangers are initially loaded in H^+ and OH^- forms but in the early stages of the run they reach equilibrium with ions in the coolant water. The cation exchanger is converted into the $H^+/K^+/NH_4^+/Li^+$ form and the anion exchanger into the BO_3^{3-} form. Potassium originates from KOH used to adjust the pH to 7.0–7.3, NH_4^+ from the addition of ammonia and lithium from the neutron-induced nuclear reaction, $^{10}B(n, \alpha)^7Li$. The flow through both these systems is 20 $m^3\,h^{-1}$, which is about 10% of the total volume of the primary circuit water. Resins in the beds are replaced approximately once a year. Spent ion exchangers are stored in stainless steel tanks and will in the future be solidified for final disposal, possibly by direct incorporation in concrete.

Deep beds containing ion exchange resins in the bead form remove both ions and particles. Removal of ^{137}Cs is practically 100%. In eight Swedish BWR plants the removal efficiency for corrosion prod-

ucts has been found to be about 95% for copper and chromium, 85–95% for cobalt and zinc and 80–90% for iron and nickel.

Polishing of Steam Condensate

In BWRs, the primary circuit water is boiling and the steam goes directly to turbines, after which it is condensed back to water and recirculated in the reactor vessel. This condensate is cleaned with ion exchanger filters. At the Olkiluoto NPP the condensate (60°C) goes through seven parallel filter units. Each unit has 25 L polypropylene pre-coat filter elements, which are coated with powdered anion and cation resins in a ratio of 1 : 2 or 1 : 3. The amount of resins in the seven units totals about 150–200 kg. Ion exchangers on the filters are replaced every 40–60 days. The primary purpose of the clean-up system is to remove ionic and particulate contaminants from the condensate. The removal efficiency for ionic radioactive species is higher than 90% and for particulate corrosion products 40–95%. In cases of leakages in the condenser, the clean-up system should also be able to remove ionic contaminants from the condenser coolant, which, in the case of the Olkiluoto NPP, is sea water.

In PWRs, condensate polishing is not important in removing radioactive contaminants because the condenser is located in the secondary circuit. The need for radioactivity removal from the condensate arises only if there is a leakage in the steam generator. The purpose of the condensate polishing, therefore, is usually the removal of corrosion products and corrosive agents.

Purification of Spent Fuel Storage Pond Water

Spent nuclear fuel is stored in water-filled ponds for several years after removal from the reactor. The water becomes contaminated because there is a large amount of particulate matter on the surface of fuel elements and because there are leakages of fission products through the fuel element cladding. In order to remove these contaminants, as well as the corrosive agents, the pond water is circulated through ion exchange filters. At the Olkiluoto NPP, fuel pond waters are purified with pre-coat filters in which the filter elements have been coated with H^+- and OH^--form resins in the ratio of 3 : 1. The flow through the filters is 180 $m^3\,h^{-1}$. At the Loviisa NPP there are separate 2 m^3 cation and anion exchanger beds in H^+ and BO_3^{3-} forms, respectively, and the particle removal is accomplished with mechanical filters. The flow rate is 18–40 $m^3\,h^{-1}$.

Treatment of Radioactive Waste Solutions

Low- and medium-activity waste solutions, originating from various sources such as leakages from primary circuit, drainage waters, decontamination solutions, laundries, etc., are usually concentrated by evaporation or solidified by precipitation or by ion exchange. The most important radionuclides in power plant waste solutions are usually ^{137}Cs and ^{60}Co. At the Olkiluoto NPP most waste solutions are solidified with ordinary ion exchange resins, and both deep beds and pre-coat filters are used. After removal of radioactivity by the resins, they are dried and mixed with bitumen in the ratio of 1 : 1, and finally cast into 200 L steel drums for final disposal.

The number of novel ion exchange applications in nuclear waste management has been increasing since the late 1980s. Evaporators have been replaced by ion exchange processes and more selective ion exchangers, especially zeolites, have been introduced into separation processes. There are two main advantages in using selective ion exchange materials: firstly, reduction in final waste volumes and thus in waste disposal costs; and, secondly, reduction in environmental discharges of radioactivity. In 1986–87 Duratek Co., for example, replaced evaporators at four PWRs in the USA with ion exchange units. In these units there are five 0.85 m^3 columns in series, packed with both conventional ion exchange resins and novel ion-selective materials. The burial volume reduction, obtained with these new systems, was 94–95% and costs decreased by 33–77%. The decontamination factors, however, were only moderate being 15–20 for caesium and 4–24 for cobalt. Decontamination factor (DF) is the ratio of initial solution activity to the activity of purified solution.

At the Catawba NPP, USA, organic resins were replaced in 1987 with a natural zeolite, clinoptilolite, in the treatment of low-level nuclear waste solutions. Clinoptilolite is an aluminium silicate mineral with the ideal composition of $(Na_2K_2)O \cdot Al_2O_3 \cdot 10SiO_2 \cdot 8H_2O$, where sodium and potassium ions are exchangeable for caesium. In column operation with 0.7 m^3 beds, caesium breakthrough typically occurs at 6000 bed volumes, compared to 1300 bed volumes obtained earlier with organic resins. In the laboratory studies, which were made to select the best ion exchange material, it was found that chabazite and mordenite zeolites worked as effectively as clinoptilolite, but the latter was chosen because of its lower price. Zeolites are used also at other NPPs in the USA for the removal of caesium for low-activity waste solutions.

Zeolites were also used at the Three Mile Island NPP, USA, for the decontamination of highly active waste solution from the reactor accident in 1979. 2780 m^3 of waste solution, which had ^{137}Cs and ^{90}Sr as major radioactive contaminants, were processed with an ion exchange system having four 230 L

zeolite columns in series. The columns contained two zeolites, IONSIV IE-96 and IONSIV A-51 (UOP, USA), in the ratio of 3 : 2. IE-96 has a Si/Al ratio of 2 : 3, typical for zeolite Y, and was selected because of its selectivity to caesium; A-51 has a Si/Al ratio of 1 : 1, typical for zeolites A and X, and was found to be selective for strontium. In total 10 columns containing some 60 000 Ci of caesium and strontium, were obtained from the process. The zeolites were vitrified for final disposal by adding glass-forming agents and heating at 1050°C.

In the 1990s a new, extremely selective ion exchange material for caesium separation, a transition metal hexacyanoferrate product CsTreat® (Selion, Finland), has been used at nuclear power plants. The general formula of transition metal hexacyanoferrates is $A_x[M_zFe(CN)_6]xH_2O$, where M is a transition metal, such as cobalt, nickel or zinc, and A is the exchangeable alkali metal (Na, K). Transition metal hexacyanoferrates have long been known as superior ion exchangers for caesium compared with organic resins and zeolites. The first application, however, using granular hexacyanoferrate in packed bed columns, was commenced in 1992 at the Loviisa NPP, Finland. The solutions treated are evaporator concentrates, which are highly alkaline and contain very high concentrations of inactive salts, typically sodium at 3 mol L^{-1} and potassium at one-tenth of this value. These types of solutions would cause instant breakthrough of caesium from zeolite and organic resin beds. In the first full-scale run, one 8 L hexacyanoferrate column processed 182 m^3 of waste solution with a decontamination factor of 2000. Thus the volume reduction obtained by this method was 23 000. Another application of CsTreat® is the removal of caesium from dilute salt solutions (Na 100–300 ppm, K 10–20 ppm, Ca 20–60 ppm) at Callaway NPP, USA, where it replaces an evaporator system. Since there are also other waste components to be removed the system contains, in addition to a 250 L CsTreat® bed, mechanical filters, a charcoal bed and a mixed resin bed. During the first eight months the system purified 1800 m^3 (7000 bed volumes) of waste effluents. The ^{137}Cs level in the purified solution was most of the time below the detection limit or at least below the target limit of 2 Bq L^{-1} (5×10^{-7} μCi mL^{-1}). The expected additional lifetime of the bed is as long as 7 years.

Successes comparable to those with cesium removal have not been obtained for cobalt. Most waste solutions containing ^{60}Co are neutral or alkaline and usually the cobalt does not exist only in the divalent cation form. The forms in which the radioactive cobalt does exist are not exactly known but it is thought to be present, in addition to divalent cations, as colloids, hydrolysation products and complexes. The most widely and successfully used separation materials for cobalt have been activated carbons. The uptake mechanism is rather complex and varies from product to product but probably activated carbons act as multifunctional materials, including ion exchange, complexation and adsorption.

For the more effective separation of activation/corrosion products ^{60}Co and ^{65}Zn, a new organic resin Diphonix has been employed at Millstone NPP, USA, since 1995. Diphonix (Eichrom Industries, USA) has a poly(styrene–divinylbenzene) matrix but the functional groups are chelating diphosphonic groups ($-(PO_3)_2^{2-}$). In addition there are sulfonic acid groups which improve the kinetics of ion exchange. In tests prior to installation of full-scale Diphonix beds at Millstone, decontamination factors (DF) for ^{60}Co and ^{65}Zn were 100 and below when a Diphonix was used alone. Combining an anion exchange resin bed with Diphonix bed increased the DF up to 1000. The processing capacity of the Diphonix bed for ^{60}Co and ^{65}Zn was at least 6000 bed volumes, which is at least 3–10 times higher than that obtained with the previously used ordinary mixed bed system.

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Ion Exchange Processes at Nuclear Fuel Reprocessing Plants

Spent nuclear fuel contains about 96% uranium, 3% fission products, 1% plutonium and less than 0.1% other transuranium elements. In reprocessing the fissile material, uranium and plutonium are separated from fission products and from other actinides and recycled for the production of nuclear fuel for reactors. The main separation process utilizes solvent extraction and most reprocessing plants use the Purex process. As the first organic ion exchange resins became available in the 1940s, reprocessing schemes using ion exchange in the main process were designed but were never used due to the poor decontamination factors achieved. Today, ion exchange is used at reprocessing plants only in the secondary waste effluent treatment and separation streams.

Separation Processes

The most important use of ion exchange in the separation processes is the purification of plutonium solutions, which can be carried out with both cation and anion exchangers. Anion exchange processes, however, yield better decontamination from impurities. At high nitric acid concentrations plutonium forms the hexanitro complex anion $Pu(NO_3)_6^{2-}$, which can

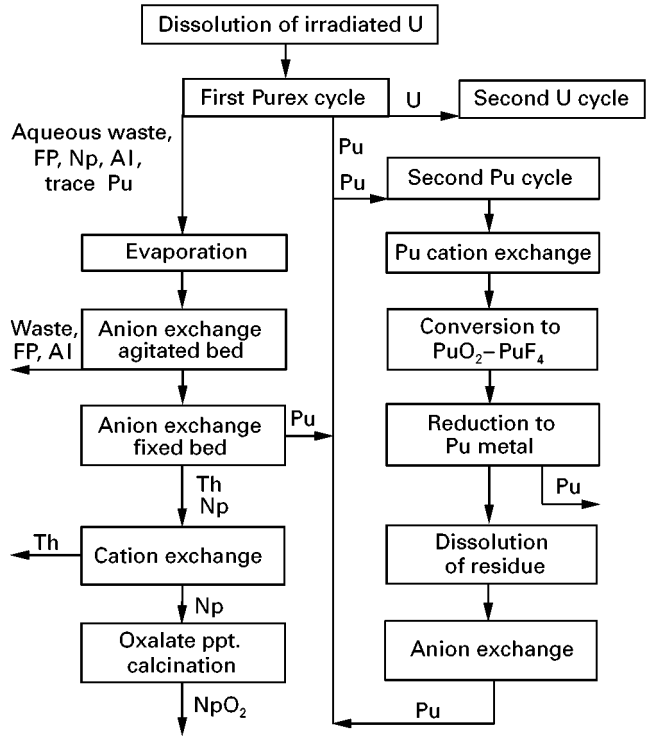

Figure 2 Ion exchange processes in the reprocessing of spent uranium fuel at the Savannah River Plant, USA.

be sorbed on an anion exchange resin in the following way:

$$Pu(NO_3)_6^{2-} + R(NO_3)_2 \rightleftharpoons RPu(NO_3)_6 + 2NO_3^- \quad [2]$$

The optimum nitric acid concentration is 7 mol L^{-1} Plutonium can be eluted from the resin with diluted nitric acid (0.35 mol L^{-1}) as the hexanitro complex is destroyed. The decontamination factor for all other elements but neptunium is very good. Plutonium can be purified from neptunium by eluting with 5.5 mol L^{-1} HNO_3 containing iron(II) sulfamate and hydrazine, instead of 0.35 mol L^{-1} HNO_3. Plutonium is reduced to Pu(III) and elutes from the column, while Np(IV) remains.

Anion and cation exchange processes can also be used for the separation of plutonium and neptunium from the high-level waste solutions of the Purex process (**Figure 2**). Plutonium is recycled to the Purex process and neptunium turned into NpO_2 to be used as irradiation targets.

Treatment of Radioactive Waste Solutions

The high activity waste effluents from civilian reprocessing plants are usually calcined and vitrified for final disposal. In the 1970s and 1980s studies were carried out on the use of inorganic ion exchangers, zeolites and sodium titanate, in the solidification of highly active waste solutions but no such processes are currently employed. In the late 1980s a zeolite IONSIV IE-96 was, however, used at West Valley reprocessing plant in New York for the removal of ^{137}Cs in 2100 m^3 of highly active neutralized Purex-process-derived waste solution. In total about 30 columns of 1.7 m^3 volume were obtained, the volume reduction thus being about 40-fold. The decontamination factor was higher than 10 000. Zeolite, together with the sludge from the tank bottom, was vitrified for final disposal.

Starting in 1997, the Japan Atomic Energy Research Institute (JAERI) inaugurated the first use at reprocessing plants of highly selective inorganic ion exchange materials in packed bed columns for the removal of ^{137}Cs and ^{90}Sr from reprocessing waste effluents and the process has worked successfully. In this pilot-scale process 2 L columns are packed in the ratio of 1 : 1 with the hexacyanoferrate product CsTreat® and a sodium titanate product SrTreat® (Selion, Finland) which is a highly selective ion exchanger for strontium in alkaline media and efficiently takes up other multivalent radionuclides. In laboratory tests with JAERI simulant (pH 10, 2.4 mol L^{-1} $NaNO_3$) the average decontamination factor of SrTreat® for strontium was 8400 at 1500

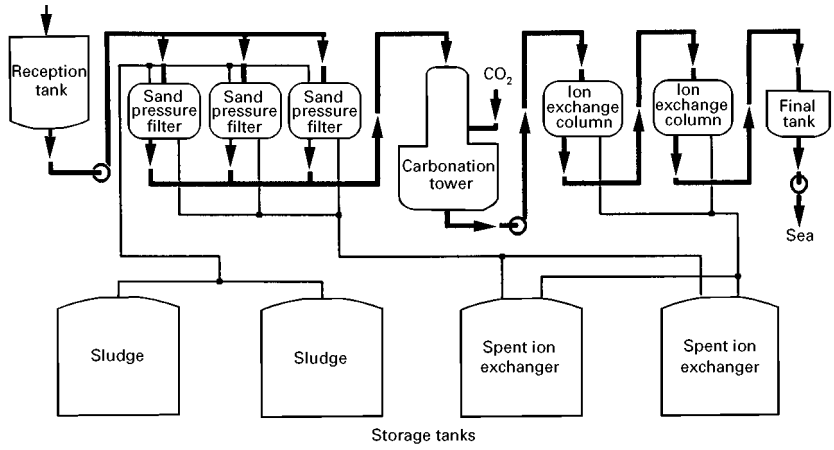

Figure 3 Simplified process flow diagram for the Site Ion Exchange Effluent Plant (SIXEP) at Sellafield, UK.

bed volumes. In other tests SrTreat® has also been shown to take up strontium most efficiently from military waste effluents (see below) which represent the most severe conditions where ion exchange can be considered for use in waste management.

In 1985 the Site Ion Exchange Effluent Plant (SIXEP), using the natural clinoptilolite zeolite for the removal of caesium and strontium from spent fuel pond waters, was put into operation at the BNFL Sellafield reprocessing plant in the UK. Spent fuel to be reprocessed is stored in water-filled storage ponds and some 3600 m^3 of the pond water have to be purged every day to keep the radiation in the ponds at an acceptable level. From this water, containing radioactive caesium and strontium, as well as activated corrosion products, particulate matter is first removed in sand filters and the pH is lowered with CO_2 from 11.5 to 8.0 to avoid the dissolution of the zeolite exchanger. Finally, the solution is passed through two beds in series, both columns filled with 10 m^3 of zeolite (**Figure 3**). The plant annually processes 700 000 m^3 of pond water, containing 17 000 Ci activity. The decontamination factors are typically 2000 and 500 for caesium and strontium, respectively, and the plant treats 20 000 bed volumes per change of zeolite. The yearly consumption of zeolite is 40 m^3.

At the Sellafield plant there is also another major waste treatment process utilizing ion exchange, the Enhanced Actinide Removal Plant (EARP), commissioned in 1994. From the mainly medium activity solutions the alpha nuclides are removed by increasing the pH to 10–11, which causes the precipitation of iron hydroxides and subsequently practically all actinides. Solid/liquid separation is accomplished with cross-flow filtration through ceramic membranes. The removal of caesium is carried out by addition of preformed nickel hexacyanoferrate sludge, which removes caesium by ion exchange and yields moderate decontamination factors of 10–50. This way of using selective ion exchangers, called seeded ultrafiltration, is well suited to combination with coprecipitation with ferric floc, but in general it is much less efficient when compared with the use of exchangers in packed bed columns, taking into account both decontamination factors and processing capacities.

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Decontamination of Military Waste Effluents

Especially in the USA and Russia there are huge amounts of highly active waste effluents, originating from nuclear weapons programmes, stored in tanks, a large number of which are leaking or expected to leak. The US Department of Energy has launched a long-term programme to treat and solidify tank wastes, which consist of salt cakes and sludges in the tank bottoms and supernatants above. In total, there are 300 000 m^3 of tank wastes, especially at the Hanford and Savannah River sites. Supernatants are highly alkaline, their pH being above 14, and the concentration of salts is very high, for example that of sodium is as high as 7 mol L^{-1}. The objective is to separate the main soluble radionuclides, ^{137}Cs, ^{90}Sr and ^{99}Tc, to minimize the volume of highly active waste to be disposed of. It is expected that ion exchange will be the main process used to do this. The extreme conditions in the solutions impose the most stringent requirements on the exchangers, considering both selectivity and chemical stability. Development of materials for tank waste remediation is discussed in the next section.

New Developments in Ion Exchange Materials

In the development of nuclear grade ion exchange resins, used in primary coolant and condensate purification, the main effort has been to decrease the fractions of leachables, both resin fragments and ionic leachables. In the development of ion exchange materials for waste treatment, where ordinary organic resins are mostly ruled out due to their low selectivities, the most important objectives have been:

1. To obtain highly selective exchanger materials for certain radionuclides.
2. To obtain ion exchange materials stable and capable of ion exchange in highly acidic or highly alkaline media.
3. To obtain ion exchangers in granular or bead forms suitable for packed bed column operations.

The highest selectivities have been found with inorganic ion exchangers. The biggest effort in developing novel ion exchange materials for radionuclide removal has been devoted to caesium-selective exchangers. In the mid-1980s zeolites were the first generation of caesium-selective exchangers. Thereafter, a wide variety of exchangers have been studied for this purpose; transition metal hexacyanoferrates, such as CsTreat® discussed earlier, have the highest selectivity for caesium (**Table 1**).

Utilization of zeolites and CsTreat® has been discussed above. Crystalline silicotitanate CST (UOP, USA) has been developed during the 1990s by optimizing the Si/Ti ratio in the exchanger and using additional metals ions, such as niobium, in the structure of the layered material. The most important possible utilization of CST is the remediation of US tank wastes, since CST has been reported to be stable in their extremely alkaline environments and to be efficient for the uptake of both caesium and strontium from the supernatants. Many other inorganic ion exchangers, especially mixed oxides, have been developed and commercialized by Allied Signal, USA.

Table 1 Selectivity coefficients of Cs/Na exchange in commercial Cs-selective ion exchange materials

Ion exchanger	*Selectivity coefficient*
Sulfonic acid resin	< 10
Mordenite (zeolite)	450
Resorcinol formaldehyde resin (SRL)	11 400
Silicotitanate (CST)	18 000
Hexacyanoferrate (CsTreat®)	1 500 000

A wide variety of chelating resins have been developed and tested for the separation of transition metal ions from solution. Of these, only a few resins, particularly iminodiacetic acid [R–N–$(CH_2–COOH)_2$] and aminophosphonate (R–NH–$CH_2–PO_3H_2$), are manufactured commercially but no applications in the nuclear industry have been reported. The only exception is the Diphonix resin discussed above. The company manufacturing Diphonix, Eichrom Industries, also produces several other radionuclide-selective resins. These 'extraction chromatographic resins' are mainly based on the incorporation of complexing agents, known to be efficient in solvent extraction processes, into the solid resin matrix so that they can be used in packed bed columns. An example of these resins is the SrResin which contains a strontium-selective crown ether in the resin matrix. The high prices of these chromatographic resins are likely to limit their use to analytical applications.

^{99}Tc is an important radionuclide in high activity waste effluents due to its very long half-life. Technetium is mainly present as a pertechnetate anion TcO_4^- and is difficult to remove. No really selective ion exchanger has so far been developed for the effective separation of technetium from waste effluents. However, the capability of ordinary anion resins to take up technetium has been improved by modifying the side chains in the functional groups –R–$N(C_xH_y)_3^+$ of strongly basic anion exchange resins. For example, compared with a commercial resin containing ethyl groups as C_xH_y, a test resin containing both hexyl and propyl groups removed TcO_4^- from ground water much more efficiently, the processing capacity being more than $\times 30$ higher.

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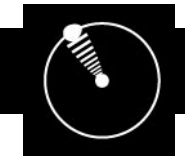
NUCLEIC ACIDS



Centrifugation

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Introduction

Centrifugation has been applied to nucleic acid isolation and purification through numerous protocols which, at some level, contain elements of one or more of three basic techniques: isopycnic or density equilibrium separation, phenol–chloroform extraction, and differential precipitation. Even if we consider only the protocols that are in current use, numerous variations on these appear in the literature. These variations result from the intended use of the product, the required purity from specific contaminants, the cost and throughput goals of the technique, and often the author's personal preferences. This article will make no attempt to cover all variations but will instead illustrate by example the basic forms of centrifuge-based techniques for nucleic acid separation as they are presently used. A rough guide to these three basic techniques and their applications is contained in **Table 1**. Each of these will subsequently be described separately.

Recent demands imposed on nucleic acid purifications by large scale DNA sequencing operations have led to the development, and increased use of filtration-based purification methods for high throughput separations. Though the cost of the filter membranes required for these separations is much higher than the cost of centrifugation, the throughput and case of automation of the membrane based methods make them preferable in many situations. Recent developments in automation of centrifugation, discussed in the last section of this article, may reverse this trend.

Isopycnic Separations

General Principle

Isopycnic separations rely on the balancing of the buoyant and centrifugal forces acting on a submerged sample during centrifugation. When a sample of density ρ_s and effective volume V is placed in a medium of density ρ_m in the presence of a centrifugal field a, the sample feels an upward buoyant force $F_b = \rho_m Va$, and an opposing centrifugal force $F_c = \rho_s Va$. Consequently, the sample will move 'up' toward the rotation axis if $\rho_s < \rho_m$ and 'down' if $\rho_s > \rho_m$. This motion terminates when the sample reaches the boundary of the medium or when it enters a region of the medium were $\rho_s = \rho_m$. Based on this principle, if a sample container is filled with a medium whose density increases gradually in the downward direction, a sample injected in this medium will migrate to the region of the medium that matches the sample density (provided such a region exists). This location is known as the isopycnic point of the sample.

Samples may therefore be separated based on their densities provided a medium is found that can be formed into a density gradient and whose density range includes that of the sample. One of the criteria in the selection of separation media for a specific sample is to ensure that this condition is met.

After a substantial migration period (often over a day), the sample fractions of different densities can be observed as bands within the medium. Extraction of these bands is performed by puncturing the centrifuge tube with a hypodermic needle and withdrawing the desired band. The resolution provided by this method is a function of the separation medium and the relative density difference in the fractions to be separated.

In the case of nucleic acids, RNA and DNA exhibit very different densities in aqueous solutions and therefore can be separated. Cesium salt solutions are typically used as the separation medium since in

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